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Materials & Molecular Research Division

Published in the Institute of Physics Conference Series
No. 52, Chapter 5, 1980, on Electron Microscopy and Analysis

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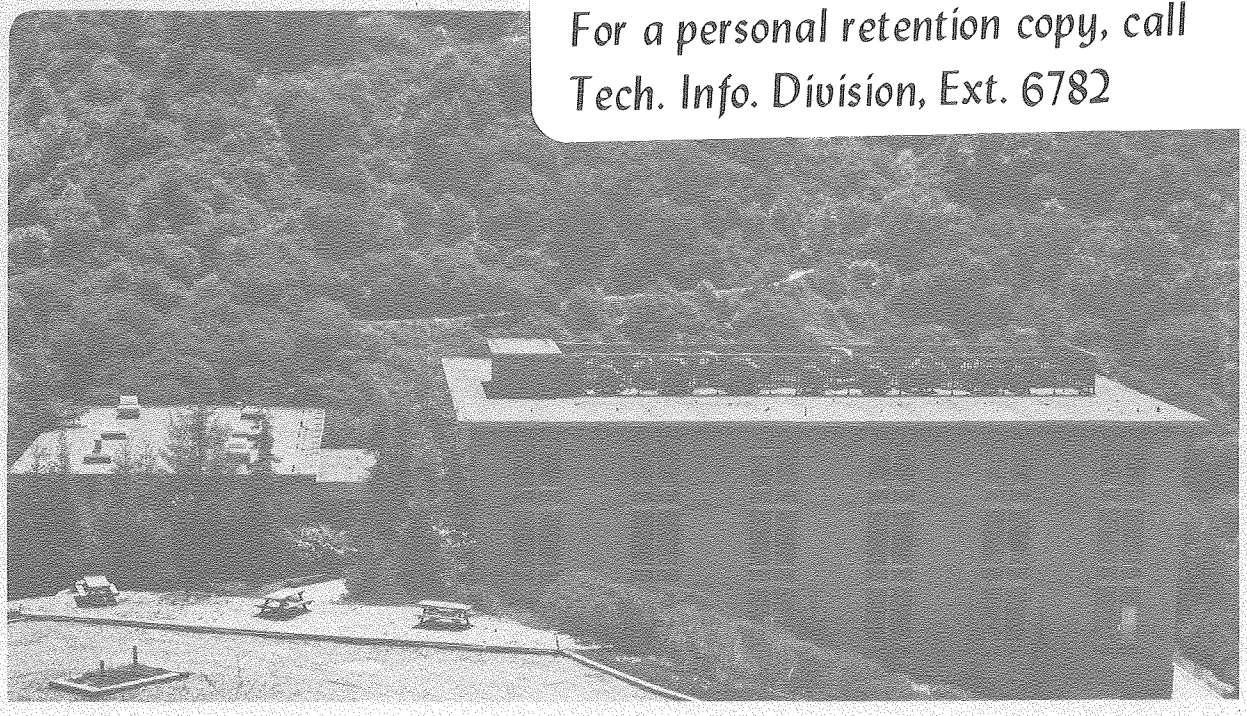
J. Y. Laval and K. H. Westmacott

January 1980



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

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ELECTRON BEAM SENSITIVITY AND STRUCTURE OF THE GLASSY PHASE OF CERAMICS

J.Y. Laval* and K.H. Westmacott

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California
Berkeley, California, 94720

1. Introduction

The electron beam sensitivity of glassy ceramics was reviewed. It was shown that the glassy phase resulting from the segregation of additives such as CaO or MgO at the grain boundaries was highly sensitive to the electron beam. We have reported elsewhere that the electron damage kinetics corresponds to an ionization process (Laval, Westmacott, 1979). This ionization process was discussed in terms of chemical bondings and ionic states, and by referring to the soda-glass structure. From these considerations new insights into the structure of the glassy phase were obtained.

2. Observations

When a silicon nitride fluxed with MgO and CaO was observed by transmission electron microscopy at 100 KeV, a mottled contrast developed specifically on the glassy phase (Fig.1a) as was first noted by Drew and Lewis (1974) at 200 KeV. It was thus possible to record a sequence of nucleation and growth of this damage. By way of example, after two minutes in an electron beam of 9 A/cm^2 the average radius of the defects was 200 Å. (Fig.1b).

When considering a manganese-zinc ferrite fluxed with CaO, it was found that the existing glassy phase was much thinner at the grain boundaries and often limited to triple points. However this intergranular glassy phase appeared to be sensitive to the electron beam too, and led to similar transformations (Fig.2). In the case of a simpler structure like a high purity zinc oxide, a glassy phase was still observed occasionally, though the total amount of glassy phase was very small. The glassy phase was again affected by the same electron irradiation damage (Fig.3).

3. Electron beam damage and sensitivity

Stereomicrographs and the contrast features were consistent with the creation of voids or gas bubbles in the bulk. Since Lineweaver (1963) evidenced an oxygen outgassing from a soda-glass irradiated by electrons at 25 KeV, it was tempting to postulate a similar damage on the glassy phase. To confirm this hypothesis we analysed the oxygen content in the glassy phase, by electron energy loss spectroscopy, on a dedicated S.T.E.M.. Fig. 4 shows that the K-edge is not

*Permanent address : Laboratoire d'Etude et de Synthèse des Microstructures, Centre National de la Recherche scientifique-E.S.P.C.I. 10, rue Vauquelin 75231 PARIS

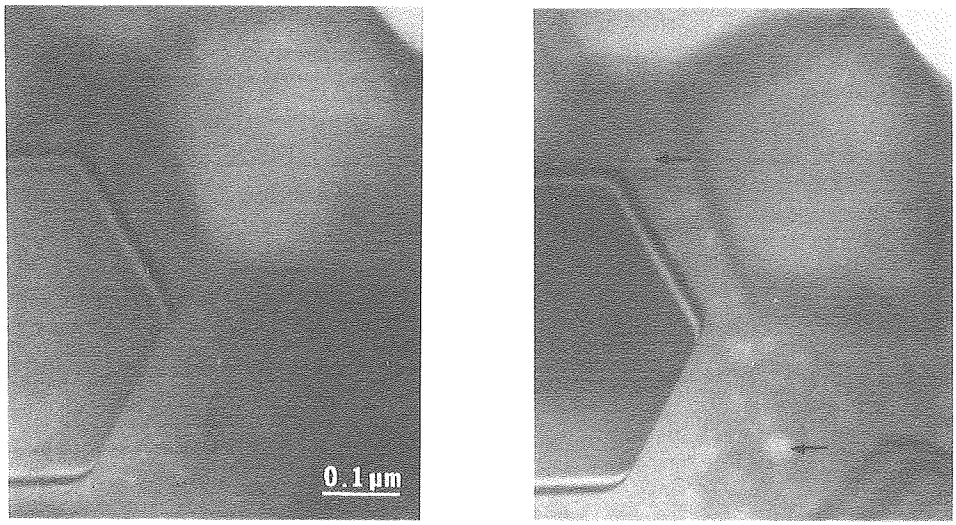

Fig 1 : Ionization damage in a MgO fluxed silicon nitride irradiated by 100 KeV electrons.
a) t = 20 secs. exposure b) t = 2 mn

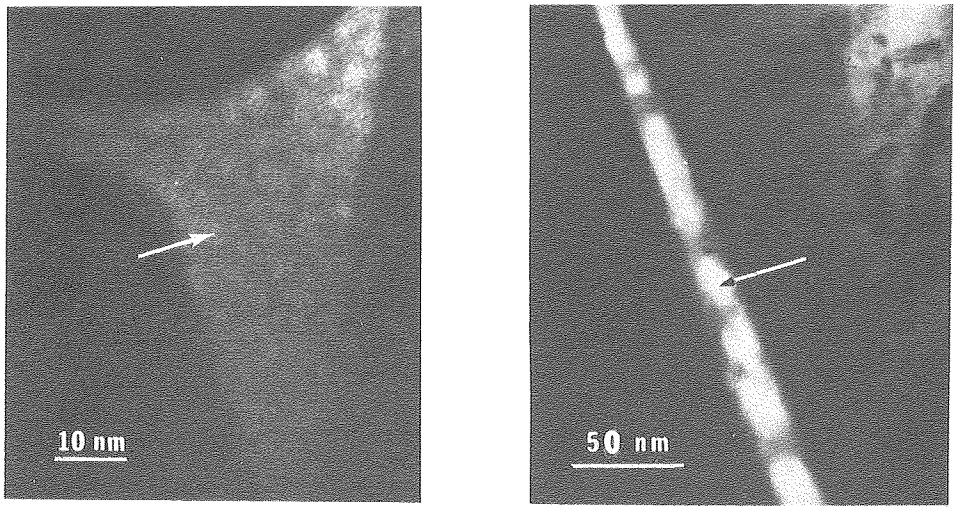

Fig 2 : Ionization damage in a CaO fluxed Mn-Zn ferrite

Fig 3 : Ionization damage in zinc oxide

(both irradiated 1 min by 125 KeV electrons - 9 A/cm^2)

visible in the ferrite matrix but appears clearly at the grain boundary (Fig. 5). We attributed this peak to a reinforcement in oxygen in the glassy phase, due to the formation of bubbles and thus interpreted the beam damage as a formation of oxygen bubbles. The damage kinetics have been described in detail elsewhere (Laval and Westmacott, 1979). The beam sensitivity is inversely proportional to the voltage and directly proportional to the intensity, which is in agreement with a primary ionization process.

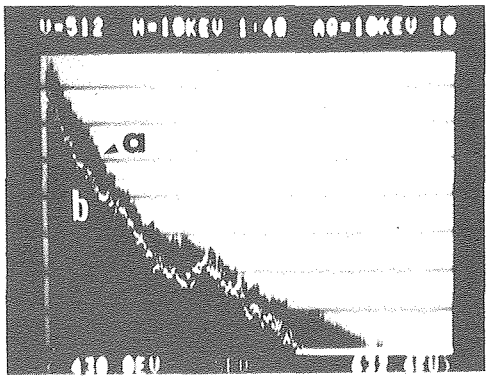

Fig 4 : Electron energy loss spectra
a) in the Mn-Zn ferrite matrix
b) at the grain boundary (fig 5)

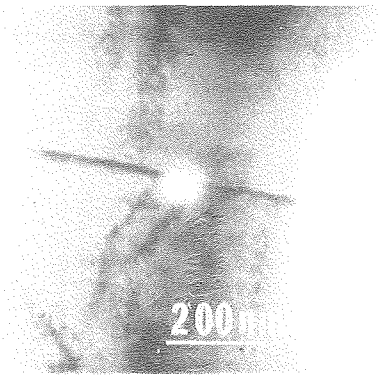

Fig 5 : Selected area corresponding to the energy loss spectrum at the grain boundary (fig 4b)

4. Ionization process and structure of the glassy phase

To analyse the ionization process, it is necessary to know the structure of the glassy phase. Fortunately, we can refer to the soda-glass structure which leads to similar damage and check whether the ionization process is compatible with the assumed structure on one hand and with the observed defects on the other. When an additive like CaO was added to a nitride or to a ferrite, it was known that this additive was likely to segregate at the grain boundaries, forming the glassy phase (Hamelin, 1972). This leads to a structure which can reasonably be inferred from the soda-glass one. Thus we assumed the creation of $Si\text{-}O^-$ dangling bonds according to Fig.6.A Ca^{++} type cation is correlated to two O^- anions. The point was to understand why this configuration was sensitive to an electron beam while the crystalline structure was not. In our opinion this complete change in sensitivity

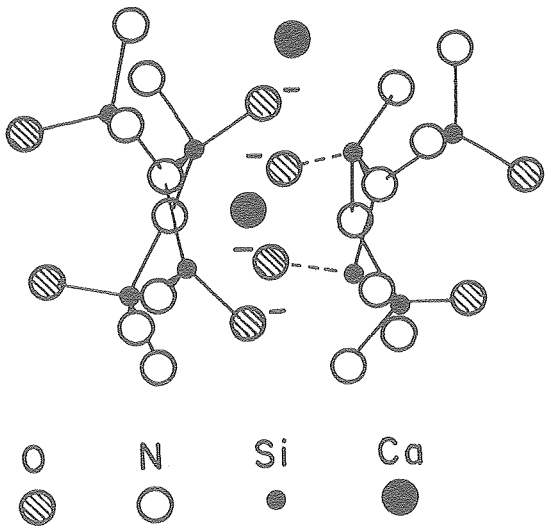

Fig 6 : Creation of $Si\text{-}O^-$ bonds by insertion of CaO in a silicon oxynitride

is the resultant of several minor effects which are all acting in the same direction, mainly : segregation of impurities leading to a more open structure, creation of non-bridging oxygen bonds, weakening of the Si-O bond in comparison with the cristalline state and change in the nature and length of the oxygen bonds. Under the electron beam, this configuration favoured an electron transfer from O to Si leading probably, on one hand to the reduction of Si to the Si^{3+} state and on the other to the oxidation of O^- to the atomic state or to a higher oxidation state.

The influence of the oxidation state of the additional cation can then be understood. If this cation is homovalent (Na, Ca or Mg for instance), the oxido-reduction may occur as described, whereas with an heterovalent cation the reaction is not possible since the oxidation of this cation to a higher valence will inhibit the oxidation of O^-. In the case of an homovalent cation, the formation of free gas may occur, due to an enhanced diffusion caused by a local increase in temperature and most likely by the transitory creation of positively charged oxygen. This effect can also be expected with other anions than oxygen as long as their electronegativity is at least comparable and provided they can lead to non-bridging bonds.

5. Conclusion

From the nature of the ionization effects it is possible to postulate which ion will lead to the damage and therefore to know the structure and the composition of the glassy phase on a nanometric scale. Thus the electron beam sensitivity of glassy ceramic enables a very thin intergranular glassy phase to be characterized and is of great value in determining the structure of the grain boundaries and of metal-oxide or glass-ceramic interfaces.

Acknowledgements

The authors are indebted to H. Fraser and P. Mochel (University of Illinois) for the electron energy loss experiments. A French Government fellowship is gratefully acknowledged by J.Y.Laval. This work was partially supported by the Division of Materials Science, Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-ENG-48.

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